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View of Oxygenates for Use as Motor Fuels and
Motor Fuel Components

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A Governmental View of Oxygenates for Use As
Motor Fuels and Motor Fuel Components

METHANOL - THE TRANSPORTATION FUEL OF THE FUTURE

for the

1983 Midyear Refining Meeting of the API

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16. ABSTRACT The Office of Mobile Sources within the Environmental Protection Agency has studied and evaluated alternative transportation fuels since its formation in 1970. This report presents the analysis which led the EPA to conclude that methanol is the most promising candidate future transportation fuel. Also included is results of completed and ongoing EPA engine/vehicle test programs and the concerns associated with the use of methanol as a transportation fuel.		
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Introduction

The Office of Mobile Sources within the Environmental Protection Agency has studied and evaluated alternative transportation fuels since its formation in 1970. EPA's responsibilities under the Clean Air Act also have necessitated a significant regulatory role dealing with transportation fuels. In particular, Section 211 of the Clean Air Act requires EPA to play a key role in the introduction of new fuels and fuel additives. Perhaps most visible was EPA's role in the introduction of unleaded gasoline to permit the use of catalytic converters on 1975 and later model year automobiles. More recently EPA has responded to a growing interest in the use of oxygenates (in particular methanol) for use in motor vehicles and for blending with gasoline.

From a technology assessment perspective, EPA has been motivated to investigate alternative transportation fuels because of concerns over diesel engine emissions. Diesel engines, which are becoming more numerous in both passenger cars and trucks, produce relatively high levels of particulate matter and oxides of nitrogen. In a sense, fuel modification can be considered as an emission control technique.

EPA studies have suggested that one alternative transportation fuel stands out above all alternatives from both environmental and economic perspectives; that fuel is methanol. Not only is methanol producible from a wide variety of raw materials, including coal, but the production technology is currently available and appears economical relative to other synfuel processes. In addition, the use of pure methanol in motor vehicles appears to have significant potential to result in improved emissions and thermal efficiency relative to alternative internal combustion engine fuels. The results of EPA's latest technology assessment are summarized in a recent report to Congress [1].

There has also been considerable interest in using alternative fuels in blends to extend petroleum supplies and raise octane ratings. Based upon the information currently available to EPA, the only prime-component oxygenates which seem potentially practical as motor vehicle fuel components are ethanol and methanol. Recent interest has concentrated on the use of methanol as a prime additive to gasoline.

Methanol as a Motor Fuel Component

Methanol, usually along with cosolvents and sometimes certain inhibitors, is being seriously considered as a motor fuel component. Most of the current attention deals with methanol as a gasoline component, although EPA has performed some preliminary investigations into the use of methanol as a diesel fuel component [2]. Methanol concentrations in gasolines of up to about 10 percent are being considered. Clearly there are certain advantages of such blends, such as an economical means of extending petroleum reserves and lower carbon monoxide emissions. However, there are several potential problems with methanol/gasoline blends including: 1) higher evaporative emissions, 2) poor vehicle driveability due to an enleanment effect, 3) material compatibility problems, 4) phase separation potential and 5) further stress on distillate availability.

Higher evaporative emissions may be a result of short-term or long-term effects. Higher short-term evaporative emissions would likely result from methanol blends due to the increased low-end volatility characteristics of methanol blends, unless appropriate volatility adjustments are made. Long-term evaporative emission concerns are associated with the possibility that methanol may reduce the effectiveness of the charcoal canister in the evaporative emission control system. Poor vehicle driveability may be experienced with some vehicles calibrated near to or lean of stoichiometric due to the additional enleanment effect of methanol/gasoline blends. While certain 1981 and later model year vehicles have closed-loop fuel control and may avoid lean driveability problems, concern remains for the other vehicles. The materials compatibility concern stems from methanol's deleterious effect on certain metals and elastomers. The materials compatibility problem can be either a short-term or a long-term concern. The tendency of phase separation in methanol/gasoline blends is well known, and can be initiated by small amounts of water. In addition to possible safety problems (i.e., vehicle stalling), phase separation would also worsen materials problems for those materials in contact with the methanol phase. Finally, using methanol in gasoline may exacerbate a potential future problem of distillate availability. Extending gasoline supplies alone would reduce the amount of oil refined and thus reduce

distillate production. There is a possibility, with the increased use of diesel engines in transportation and other demands on distillate fuels, that extending gasoline supplies through the use of methanol blends may be counterproductive.

EPA's involvement in considering these potential problems is limited to the provisions of Section 211(f)(1) of the Clean Air Act which prohibit the introduction of any new fuel or fuel additive for general use in 1975 and later model year automobiles, unless the EPA Administrator waives the restriction by determining that the new fuel or fuel additive will not cause or contribute to a failure of the vehicle emission standards. EPA has granted several methanol/gasoline waivers and intends to continue to work with interested parties to help define the constraints on the appropriate use of methanol as a motor fuel component.

Neat Methanol as a Motor Fuel

As mentioned previously, EPA's Office of Mobile Sources has studied and evaluated alternative transportation fuels for several years. The remainder of this paper: 1) presents the highlights of an analysis which led the Agency to conclude that methanol is the most promising candidate future transportation fuel, 2) updates the results of certain recently completed and ongoing EPA engine/vehicle test programs, and 3) presents and discusses some concerns associated with the widespread use of methanol as a transportation fuel.

Extensive discussion would be necessary to properly evaluate all important considerations for the various candidate alternative transportation fuels, but because of the brevity required for this paper, it must suffice to focus on the highlights which have led EPA technical analysis to date to conclude that methanol appears to be the most promising future surface transportation fuel. How the transition from the petroleum era to the methanol era can occur and when it will or should occur are important questions but are also beyond the scope of this paper.

This paper will begin with the technology and cost of producing methanol relative to other synthetic fuels from coal, our primary domestic energy resource. Only the use of coal is considered here because it will be

the key to any synthetic fuels program which intends to significantly decrease our dependence on foreign petroleum. From a broader raw material availability perspective, methanol is also attractive. Methanol is produced by reacting carbon monoxide and hydrogen over a catalyst, and processes have been in commercial use for many years. The question of whether a given material can be converted into methanol is actually one of whether it can be converted into carbon monoxide and hydrogen. Because partial oxidation of almost any carbonaceous material in the presence of steam can be made to produce carbon monoxide and hydrogen, there are a great many raw materials which can be converted into methanol. These include wood, peat, municipal solid waste, natural gas, and all grades of coal including lignite. This range of possible raw materials may offer the long-term advantage of a geographically diverse methanol fuel industry, since various feedstocks are spread across the country. However, the cost of methanol and other indirect liquefaction products from domestic resources should be significantly less from all grades of coal than from the other raw materials. Thus, in the near-term, coal would likely be the raw material of choice. While direct liquefaction processes can process subbituminous (Western) or bituminous (Eastern) coal, the economics are such that bituminous coal would likely be used. A major advantage of methanol over direct liquefaction products is that its economics appears to be less dependent on coal type.

Production and Distribution

The chemical industry already produces methanol from natural gas and residual oil, so the technology to produce methanol from synthesis gas is fully commercial. Methanol is produced from coal via indirect liquefaction, a two-step process consisting of first gasifying coal into carbon monoxide and hydrogen and then synthesizing this gas into methanol. The second step of the process, methanol synthesis, is the same regardless of the feedstock used to produce the synthesis gas. Coal gasification is also commercially proven, as first-generation gasifiers have been in operation for thirty years. However, more efficient second-generation gasifiers have been under development for over twenty years and a number of these gasifiers now appear to be ready for

commercialization. Thus, the production of methanol from coal appears to be achievable today and only waiting for the proper economic conditions.

Other indirect liquefaction processes also are commercial or near commercial. The Fischer-Tropsch process is definitely commercially proven, as full-scale plants are currently operating in South Africa using first-generation coal gasifiers. The other indirect process, the Mobil MTG process, converts methanol into gasoline. Up to the methanol conversion step, the technical feasibility of this process is the same as that for a methanol-from-coal facility, which was already described above. The final methanol-to-gasoline step is not as commercially ready, however, having been only demonstrated in small pilot plant units.

Direct liquefaction processes, on the other hand, are a number of years away from commercialization. Large pilot plant work is currently underway and progress is being made. However, significant technical problems still remain to be overcome. In addition, many of the key processing steps have not yet been integrated, but have only been tested individually. Thus, most plans call for a large-scale demonstration plant to be built to develop confidence in the entire process before any commercial plants would be planned. Overall, the direct liquefaction processes are not in the same state of commercial readiness as are the indirect liquefaction processes.

A variety of individual coal gasifier types are available but there are several properties of coal which are important in the selection of an individual gasifier. Without going into the details of the various gasifiers and coal properties and their interactions, four processes were chosen from the many considered for detailed economic analysis. These were the Texaco, the modified Winkler, the modified Lurgi, and the Koppers-Totzek processes. Synthetic gasoline was studied from methanol via the Mobil MTG process. And the Fischer-Tropsch process was used as a final means for producing transportation fuel via indirect liquefaction.

Like indirect liquefaction, numerous direct liquefaction processes could be evaluated; however, the three direct liquefaction processes chosen for detailed economic analysis were the Exxon Donor

Solvent (EDS), the H Coal, and the Solvent Refined Coal-II (SRC-II) processes.

Various results of the EPA study [1] will be summarized in this paper. First, the thermodynamic conversion efficiencies and product mixes for several coal conversion technologies are presented in Table 1. An effort has been made to put all of the efficiencies and other information presented in these comparisons on the same, and most comparable, basis. Further, the product slates were set up to maximize the amount of useable transportation fuel. The two efficiencies shown for methanol in Table 1 represent the range of efficiencies expected for the nine different gasifier/synthesis combinations considered in the EPA study. It is worth noting that the efficiency of producing methanol can be significantly improved by coproducing substitute natural gas (SNG), however, as mentioned earlier, a major criterion was to maximize the production of transportation fuels. Of course, further improvements in all the processes are possible as optimization work continues. Table 1 shows that direct liquefaction processes are projected to be somewhat more efficient than processes which would produce methanol. However, the methanol production processes yield 100 percent methanol which is considered a premium transportation fuel whereas portions of the direct liquefaction product slates are not suitable transportation fuels.

Recalling that diesel-fueled engines are more efficient than gasoline-fueled engines and that the current transportation fuel demand is shifting progressively toward diesel fuel, a synthetic gasoline product may not be most desirable. It is also important to note that the distillate produced by direct liquefaction will probably not be available for use as diesel fuel. Coal liquefaction distillates need to be severely hydrotreated to reduce the aromatic content to a sufficient degree (less than 25 percent aromatics) so that a cetane number of 36-39 can be obtained. These cetane numbers are still lower than the minimum ASTM specification for diesel fuel of 40, and well below the current national average of 46. Therefore, additives to boost the cetane number would likely be required even before severely hydrotreated coal distillate could be used as diesel fuel. This would be more severe hydrotreating than indicated in Table 1, and would therefore lower the indicated efficiencies and yields.

There have been many studies undertaken in the last few years to project the cost of producing synthetic fuels from coal. However, the conclusions from these studies vary widely and make generalized conclusions about the relative economics of producing one synthetic fuel versus another very difficult. This variability appears to be due to a number of reasons. One, the economic bases used for the various studies often differ, affecting cost by as much as 100 percent. Two, each study uses the best information available at the time of that study. Since the product mixes, efficiencies, and costs of many of these processes, especially the direct liquefaction processes, change frequently as more is understood about each process, studies performed even two or three years ago cannot be compared directly to the latest studies. This is especially true in cases where information was originally nonexistent and assumptions had to be made.

The EPA study attempted to focus on the original engineering studies to assess the reasonableness of the various cost estimates. The available designs of each process were compared to ascertain which ones were outdated or based on inaccurate assumptions. After performing this "technical screening", placing everything on the same economic basis, and adjusting for plant size, surprisingly good agreement within each process was found. Where there are still differences, these differences can usually be explained by differences in the process technologies used.

For the presentation of results, product fuel costs were normalized to two sets of economic and financial parameters. One set uses an overall annual capital charge rate (CCR) of 11.5 percent, representing utility financing, and the other an overall annual CCR of 30 percent to represent a private financing option. Each plant was also scaled up or down to a production level of 50,000 fuel-oil-equivalent barrels per day, all results were expressed in 1981 dollars, and all common costs were normalized (for coal, utilities, etc.). As an important caveat, the final answer will, of course, remain unclear until commercialization of these processes, and the conclusions presented here must be considered in this light.

Determining the economics of production of useable synthetic liquid fuels is probably the most difficult of the three economic areas; the other two being the distribution economics and the economics of use. However, the differences and uncertainties surrounding the economics of production for the various synthetic liquid fuels appear to be minor compared to the economic differences associated with the end-use of each fuel. (This will become clear later when the engine efficiencies and costs for the various alternative transportation fuels are considered.) It is most important to consider the overall efficiencies, economics and environmental impacts from the base energy form/location through final end-use (for transportation, passenger-miles or ton-miles per energy unit) when considering choices among various alternative transportation fuels. By computing the cost of producing and distributing each synfuel on a per energy basis (dollars per million Btu), the combined cost at vehicle delivery will appropriately reflect all costs up to that point. Then the cost and efficiency of utilization will allow the final comparison of overall economics.

The costs of producing finished products from several of the synthetic fuel processes studied are presented in Table 2. First, the capital cost for each process was determined and then the product cost based on the two different capital charge rates was determined. Finally, the cost of refining and upgrading the synthetic crudes is added, and the final product costs are shown in Table 2 along with the resultant product mix. The overall costs were allocated among the various products in a manner that would simulate their market demand. The conclusion from the available data is that, in general, it appears that the indirect coal liquefaction processes can produce useable transportation fuels at a lower cost than direct liquefaction technologies.

Since distribution systems already exist for gasoline, the short-term distribution economics would, of course, favor the continued use of this fuel over the introduction of methanol. Gasoline also has about twice the energy density of methanol. Thus, because transportation cost depends primarily on volume, gasoline would also be less expensive to transport per Btu on a long-term basis.

Analysis of fuel distribution costs were divided into three parts: 1) cost of distribution from refinery or plant gate (if no refining is required) to the regional distributor, 2) cost of distribution from the regional distributor to the retailer, and 3) cost of distribution by the retailer (i.e., at the service station). Our estimates of the total cost for distributing methanol are \$1.69 to \$1.88 per million Btus, and for gasoline \$1.34 per million Btus. Gasoline has a significant advantage over methanol in terms of percentage, but the absolute difference is only \$0.35-0.54 per million Btus.

All of the methanol and synthetic gasoline production processes will affect the environment to some extent, as will the distribution and storage of the fuels themselves. Coal contains many elements and compounds in addition to hydrogen and carbon, such as organic nitrogen-containing compounds, organic and inorganic sulfur, trace metals, etc. The conversion of coal to other fuels offers a number of opportunities for these pollutants to reach the environment in harmful ways, regardless of the particular conversion process used.

Focusing primarily on the differences between indirect and direct liquefaction, one potential advantage of gasification over direct liquefaction is the fact that most of the organic nitrogen and sulfur is broken down into simple compounds like ammonia and hydrogen sulfide. These are relatively easy to separate from the carbon monoxide and hydrogen which make up the major parts of the synthesis gas. Also, since the carbon monoxide and hydrogen entering the methanol synthesis unit must be essentially free of sulfur to prevent rapid catalyst deactivation, there is a built-in economic motivation for its removal.

Direct coal liquefaction, on the other hand, inherently leaves some of the sulfur and nitrogen in the liquid phase, found with the organics. The most effective technique to remove these elements is hydrogenation, which also is used to upgrade the fuel. However, hydrogenation is expensive, because of the large amounts of hydrogen consumed, and will likely be limited to only the degree that is necessary to market the fuel. If the fuel is upgraded to gasoline or high quality fuel oil, most of the sulfur and nitrogen will be removed and there should not be any significant sulfur or nitrogen emission problems. However, that portion of the synthetic crude which may

be burned with little or no refinement could contain relatively high levels of these elements and represents more of an environmental concern than gasification products.

Another difference in the potential environmental effects is in the exposure to the fuels themselves. While coal liquids are for the most part hydrocarbons and similar to petroleum, they have a higher aromatic content and some may contain significant quantities of polycyclic and heterocyclic organic compounds. Some of these compounds are definitely mutagenic in bioassays and many have produced tumors in animals. Thus, while the noncarcinogenic health effects of these materials would be similar to those of crude petroleum, they would definitely have the potential to be more carcinogenic. There is also some evidence that much of this bioactivity can be removed by moderate to severe levels of hydrogenation which would occur if high grade products were produced. Thus, again the potential hazard is dependent upon the degree of hydrogenation given the products. Indirect liquefaction products, on the other hand, do not appear to exhibit mutagenicity or carcinogenicity.

Another point which deserves mentioning is the difference between the effect of an oil spill and a methanol spill. The effects of oil spills are well known. The effects of a methanol spill are expected to be quite different, primarily because methanol is soluble in water. While high levels of methanol are toxic to fish and fauna, a methanol spill would quickly disperse to nontoxic concentrations and, particularly in water, leave little trace of its presence afterwards. Water life should be able to migrate back quickly and plant life should begin to grow back quickly, though complete renewal would take the time necessary for new plants to grow.

There are various concerns with the handling and use of methanol, and these will be discussed in a later section of the paper. While more work clearly needs to be performed in this area, the production of synthetic fuels from coal via indirect liquefaction processes appears to offer environmental advantages over the direct liquefaction processes.

Use of Methanol in Motor Vehicles

First, the final closure on the economics of using methanol in motor vehicles versus synthetic gasoline will be presented. Second, the latest information on emissions and performance (both energy efficiency and specific power) of methanol-fueled engines as compared to gasoline and diesel-fueled engines will be presented, focusing primarily upon EPA's own test programs.

The two primary effects on the economics of using a given fuel in an engine are the efficiency of the engine and its cost, including its emission control system cost. In keeping with the conservative approach used in this paper when comparing methanol to gasoline from direct coal liquefaction, a fuel efficiency advantage from methanol engines over their gasoline counterparts of only 20 percent is used. As will be discussed later, the methanol engine may well have a fuel efficiency equal to (and perhaps exceeding) that of a diesel, which is 25 to 30 percent better than a gasoline engine. A final conservative assumption that will be used is that there will be no difference in the cost of a methanol engine as compared to a gasoline engine. As will also be covered in part later, such factors as significantly higher specific power, reduced cooling system requirements, and lower emission control system cost of the methanol engine would likely give it a significant cost advantage as compared to the gasoline engine. Using these assumptions, a fuel economy of 30 mpg for the average gasoline-fueled vehicle and an average usage of 12,000 miles per year, the annual fuel savings relative to synthetic gasoline produced via indirect liquefaction (Mobil MTG process) were determined. Table 3 presents the final vehicle use economics. It should also be noted that the information presented in Table 3 assumes that all fuels were derived from bituminous coal. If a lowest feedstock-cost approach had been taken, then the economic benefits of methanol (and indirect gasoline) as compared to direct liquefaction gasoline would have been even greater than shown in Table 3.

Perhaps the most significant conclusion of this analysis is that the efficiency and cost of the optimum engine for each of the various alternative transportation fuels may have an even greater influence on the overall economics than significantly

different production efficiencies and delivered fuel prices. Based on the information currently available, methanol appears significantly superior to direct coal gasoline from both the delivered fuel price and the overall economics perspectives. Finally, it should again be stated that no comparison was made between methanol and diesel fuel since none of the coal conversion processes examined produces diesel fuel of sufficient quality for today's diesel engines.

Methanol can be burned in a wide variety of engines. EPA has both reviewed the results of other testing programs [3,4] as well as begun its own engine evaluation program [5,6,7]. There are several features of methanol that make its use in internal combustion engines especially attractive, and these characteristics are discussed in previous EPA reports. This paper will focus on the results of some of the most recent EPA programs to characterize the emissions and efficiency of methanol-fueled engines and vehicles.

Methanol-fueled engines promise improved emission characteristics over gasoline and diesel engines in a number of areas. Especially important are low emissions of nitrogen oxides (NOx) and an absence of emissions of particulate matter, heavy organics and sulfur-bearing compounds. These emissions advantages may become even more significant in the future, as the quality of crude oil, and diesel fuel in particular, declines. This is especially important for diesel fuel, since a reduction in quality will likely result in an increase in emissions, especially particulate matter.

Another potential benefit of methanol is the possibility that the exhaust catalyst could be of the base metal variety, such as copper, chromium, or nickel, and not require noble metals, such as platinum and palladium. Unlike gasoline, methanol does not contain any sulfur or trace lead, which degrade base metal catalysts. This could significantly reduce the cost of the catalytic converter system. This change could also improve the country's balance of payments, since all noble metals must currently be imported. While some base metals are also imported, their value would be significantly less and still produce a net decrease in imports. Of course, it may also be possible that a noble metal catalyst with significantly less noble metal loading could still be

effective. In either case, a significant potential exists to use a lower cost catalyst with methanol-fueled vehicles.

Methanol engines, however, generally emit more aldehyde emissions than gasoline or diesel engines, including formaldehyde, a suspected carcinogen. Uncertainties exist as to whether the increases are significant, since the current level of formaldehyde emission from gasoline and diesel engines is not now thought to present a problem. Fortunately, research testing of catalytic converters has shown that they are able to remove up to and perhaps more than 90% of the aldehydes. Reducing engine-out formaldehyde emissions and optimizing catalytic reductions will undoubtedly be high priorities for automotive manufacturers.

Tables 4 and 5 present summary results from recent EPA characterization programs that have evaluated methanol-fueled engines developed by others [5,6,7]. Although these are early prototypes and are basically straightforward conversions of their gasoline/diesel counterparts, they do provide EPA with the opportunity to perform a preliminary assessment of the exhaust composition of methanol-fueled vehicles. Exhaust from each of the light-duty vehicles and heavy-duty engines tested in these programs was analyzed for each of the currently regulated pollutants: hydrocarbons, carbon monoxide, oxides of nitrogen, and particulate. Tests were performed for a range of other organic compounds such as methanol, formaldehyde, other aldehydes and ketones, and some individual hydrocarbons. In addition, several other unregulated pollutants (nitrosamines and total organic amines, ammonia, cyanide, and methyl nitrite) were measured during tests on one of the light-duty vehicles. Phenols, smoke, sulfate, and benzo(a)pyrene were also analyzed from the heavy-duty engines. The basic intent was to identify any possible emission surprises as early as possible with respect to methanol-fueled engines. The results of the test programs compare well with what would have been expected.

Since "hydrocarbons" are controlled because of their role as oxidant precursors in the urban atmosphere, the relative masses of organic emissions in gasoline and methanol exhausts are not as important as the relative photochemical reactivities of the organic species. Since the exhausts from various alternative

fuels could have significantly different photocnemical reactivities even at similar mass emission levels, specific hydrocarbon (organic) analysis of exhaust is important. For example, formaldehyde is known to be very photochemically reactive, but unburned metnanol itself is generally considered to be of low photochemical activity. As shown in Table 4, the light-duty methanol vehicles emitted more methanol and formaldehyde emissions than their gasoline counterparts, but the methanol exhausts contained almost no alkenes, aromatics, or non-methane alkanes which are the major reactive components of gasoline exhaust. Thus it is not immediately clear whether methanol exhaust would be more or less reactive than gasoline exhaust. The organic emissions from the heavy-duty methanol engine shown in Table 5 were almost exclusively unburned methanol, with only trace levels of formaldehyde and hydrocarbons, which would probably result in lower photochemical reactivity impacts compared to the baseline diesel engines. It must be noted that the methanol heavy-duty engine was equipped with an oxidation catalyst while the diesel engines had no form of aftertreatment.

Both the CO and NOx results were mixed from the light-duty vehicle tests (Table 4), with methanol sometimes increasing and sometimes decreasing these emissions. However, as with all the emissions, both the gasoline-fueled and methanol-fueled vehicles emitted very low emission levels, as they were all calibrated to meet the very stringent future California emission standards. Therefore, considering the level of control, the differences observed are quite small in absolute terms. One significant observation is that a trade-off seemed to be occurring between NOx emissions and energy efficiency. Although optimum methanol combustion would be expected to occur at very lean operation, both of the methanol light-duty vehicles utilized three-way catalytic converters and thus were forced to operate at very near stoichiometric conditions so that the NOx reduction catalyst would perform well. The methanol-fueled Escort showed no significant difference in energy efficiency at very low NOx levels, while the methanol-fueled Rabbit showed a significant increase in efficiency but at higher NOx levels. The methanol-fueled Escort was calibrated with more spark retard than the Raabbit thus resulting in lower NOx and relative efficiency. Emissions of particulate and unregulated compounds such as ammonia,

cyanide, and organic amines are consistently lower from the methanol-fueled vehicles than from similar gasoline-fueled vehicles. No surprises appeared in the extensive characterization program of the methanol-fueled vehicles. However, the optimum emissions and efficiency configurations for methanol-fueled vehicles may very likely be different from the vehicles tested in this program.

EPA has several contracted methanol engine optimization programs currently underway including projects with Ford Motor Company to optimize the Ford PROCO engine with methanol and with Ricardo Consulting Engineers to evaluate methanol performance with the Ricardo HRCC (high compression ratio, compact chamber) combustion system when fueled with methanol, as well as an in-house program at the Ann Arbor laboratory. While the in-house program is only a modest effort, preliminary results from the program are encouraging. The in-house program is first focusing on the determination of optimum engine efficiency and emission configurations, with the second phase to be a final emission control system integration and vehicle testing. A parallel methanol exhaust aftertreatment project is also underway and preliminary results from this effort will be presented later. It is also important to point out that development/optimization activities for methanol engines are in a very early phase, as compared to gasoline and diesel engines. Therefore, it is reasonable to expect additional significant improvements in any methanol efficiency or emission results that are now available.

Figures 1 and 2 present thermal efficiency values at two different power settings from one of the engines being evaluated in the EPA in-house program (the Nissan NAPS-2) compared to several advanced technology passenger car engines. (Other in-house engines show similar results with methanol, but the NAPS-2 engine has more versatility in parameter control and is receiving most of our experimental focus.) The NAPS-2 engine represents an advanced technology Otto-cycle engine, having both low friction and fast burn characteristics. The Volkswagen Rabbit turbocharged diesel engine is presented to represent state-of-the-art indirect injection passenger car engine technology. The turbocharged, direct injection Sofim diesel engine is representative of the best efficiency characteristics in research passenger car diesel engines. As can be seen, the methanol NAPS-2

is more efficient than any of the other advanced technology engines shown. The methanol results from the NAPS-2 engine, while very impressive, represent only simple compression ratio changes from the gasoline engine and parameter optimization for methanol fuel. Several alternative configurations are being evaluated for methanol which include water/methanol blends for reduced NOx emissions and possibly improved efficiency and specific power, partial methanol dissociation for increased efficiency and reduced emissions, and turbocharger optimization. The methanol-fueled NAPS-2 engine also produces about 25 percent more power than its gasoline configuration.

Figures 3 and 4 present preliminary results from the EPA/Ricardo contract. These results come from a 1.5 liter HRCC engine Ricardo prepared for EPA. The engine has a 13:1 compression ratio, with methanol results being generated with the engine equipped with a very simple single barrel carburetor while the gasoline results are taken from the same engine fitted with an improved two barrel carburetor. The part-load conditions presented are within the range of operating conditions commonly encountered in a normal vehicle application. Although these results are from the same engine, methanol operation generally produced efficiency improvements of 4 to 6 percent over the gasoline fuel. These gains may be due to the effects of lower combustion temperatures when using methanol, the greater number of moles of combustion products per mole of fuel for methanol, and/or the faster combustion characteristics of methanol (higher flame speeds). The NOx emissions from methanol are significantly lower than with gasoline, and achieve very low levels at lean equivalence ratios where methanol combustion still appeared stable. In contrast, even with the HRCC engine, gasoline combustion appeared unstable at equivalence ratios lean enough to get significantly lowered NOx levels. A significant issue for methanol-fueled engines designed for very low NOx levels will be whether good vehicle driveability can be achieved when operating at an equivalence ratio near 0.7.

Another interesting result of the Ricardo study is the assessment of idle performance. Figure 5 presents idle fuel consumption and hydrocarbon emission results for several engines. The curves for each engine represent different spark timing and equivalence ratio

settings. Of significance here is that the methanol-fueled HRCC engine idle fuel consumption is one-half that of the standard production gasoline engine, and within the range for production diesel engines.

If methanol-fueled engines can operate satisfactorily at lean equivalence ratios for optimum efficiency and very low NOx emissions, then oxidation catalysts (perhaps with some EGR) may be sufficient to meet stringent emission standards. As was mentioned previously, it may also be possible to use low cost oxidation catalysts with methanol-fueled vehicles. The in-house test program evaluating alternative catalysts is using the methanol-fueled Volkswagen Rabbit, characterized in its stock configuration in Table 4. Table 6 presents preliminary summary data on several alternative catalysts. Early results are encouraging.

Concerns Regarding Methanol Use

Several studies have been performed which assess the environmental effects of synfuel use [1,8,9]. However, while EPA is continuing to evaluate the environmental effects of the various alternative transportation fuels production processes, this discussion will focus on the concerns with the use of methanol as a motor vehicle fuel. The discussion will address specific exhaust emission concerns as well as general health and safety concerns associated with the handling and use of methanol. The general concerns include: 1) the ingestion, inhalation and skin absorption of methanol, 2) the almost invisible flame produced when methanol burns, and 3) that the methanol vapors in the fuel tank are likely to be ignitable. Exhaust concerns include: 1) the reactivity of the methanol exhaust, 2) the inhalation of unburned methanol in the exhaust, and 3) the formaldehyde levels in the exhaust.

Methanol is highly toxic in heavy exposures, leading to blindness or death. Much of its notoriety in this area is due to people confusing it with ethanol and drinking it in large quantities. Hydrocarbon fuels, while also being toxic, do not suffer from this confusion and are not often taken internally. The absorption of methanol through the skin is also hazardous, more so than gasoline (though the presence of benzene in gasoline complicates this issue). Given

the public's rather careless use of gasoline, widespread use of methanol would pose some concerns in this area. EPA has recently performed a preliminary study on the health effects of methanol [10], and results from that study will be summarized here.

Methanol was a frequent component of liniments, perfumes, and some patent medicines well into this century. It has seen widespread use as a solvent and as a high volume chemical. While bioassay studies with methanol are limited, current results suggest that methanol is not mutagenic. Methanol can be introduced into the body through ingestion, inhalation and skin absorption, and the dose rather than the mode of introduction seems to be the most important parameter in expected health effects. Defining safe exposure and dose levels is extremely difficult because of the very large variability in individual response. In addition, the toxic effects are generally delayed (twelve to eighteen hours after dose) and may be as severe as blindness and even death. If death does occur, it is generally attributed to respiratory failure. To illustrate the wide variability and individual sensitivity to methanol ingestion, one death was reported in the literature from a dose of only 6 milliliters of methanol (about 1 teaspoon) while recovery has been reported for a 500 milliliter dose. Receiving a significant methanol dose through skin absorption is a real concern as the skin absorption rate is reported to be 0.2 milligrams per square centimeter per minute.

Inhalation studies have shown a wide range of effects. Headaches have been reportedly caused from inhaling methanol concentrations as low as 22 milligrams per cubic meter. The odor threshold may be as low as 5 milligrams per cubic meter, although some studies indicate that the odor threshold is much higher. The OSHA work place standard for methanol is 200 milligrams per cubic meter maximum. The threshold limit value (TLV) is 260 milligrams per cubic meter, with a 310 milligrams per cubic meter short-term limit. The Soviet Union has established a maximum allowable concentration in work place air of 5 milligrams per cubic meter; and 1.0 milligrams per cubic meter one-time limit and 0.5 milligrams per cubic meter average limit in populated places. Because of the wide variability in response, lower limits for the ranges of concern for methanol of 0.1 to 1.0 milliliters for ingestion and 1.0 to 3.0

milligrams per cubic meter for inhalation have been suggested [10]. Skin contact should also be avoided. While some treatment is available for methanol ingestion, it seems prudent that every reasonable effort should be made to avoid methanol ingestion, skin contact and prolonged inhalation. Several actions can be taken to address these concerns. Public education regarding the risk of methanol exposure would be fundamental. Use of the term methyl alcohol should probably be avoided; perhaps a non-alcohol fuel name would be wise. Warning labels on dispensers and containers would need to be reviewed for effectiveness.

Another concern with methanol use is that the methanol flame is essentially invisible in daylight. Although methanol flames are cooler than gasoline flames and extinguish with water, methanol/water concentrations down to about 26 percent methanol are still flammable. On the other hand, methanol has a higher flashpoint and ignition temperature than gasoline, thus in open air it is considered less of a fire hazard than gasoline.

Due to methanol's volatility characteristics, the vapors in a methanol tank would be expected to be flammable. However, flame arresters in the tank filler neck or bladder tanks seem capable of mitigating this concern. Also, the electrical conductivity of methanol is higher than for gasoline which reduces the problem of static discharge causing ignition.

The possibility of using additives with methanol should be investigated to help alleviate these concerns. Methanol additives should be sought which would: 1) cause vomiting if ingested, 2) make ingestion, inhalation and skin contact unattractive (e.g., unpleasant smell, or dye), and 3) provide a visible flame.

Concerns with the emission products from methanol combustion center largely around the question of the reactivity of the exhaust and formaldehyde emissions. The reactivity of the exhaust, which is primarily methanol, was discussed earlier and still needs further study. While most researchers agree that methanol has a low reactivity and therefore little

potential for ozone formation, additional modeling and smog chamber work should be conducted to resolve this question.

EPA has also performed a preliminary formaldehyde health effects study [11]. Formaldehyde is a photochemically active organic and may play a larger role in methanol exhaust reactivity than the emissions of unburned methanol. Formaldehyde also has toxic effects with a TLV of 3.0 milligrams per cubic meter. The bottom end of a range of concern for formaldehyde would probably be between 0.06 milligrams per cubic meter and 0.2 milligrams per cubic meter [11]. In addition, formaldehyde has been shown to cause cancer in laboratory animals. Additional work needs to be conducted to assess the potential impact of formaldehyde emissions from methanol-fueled vehicles. As mentioned previously, low formaldehyde exhaust emission levels appear available with exhaust catalysts. To put the formaldehyde emission concern in perspective, Table 7 shows formaldehyde emissions for a variety of passenger cars. It can be seen that formaldehyde emissions from conventional catalyst equipped methanol-fueled vehicles are equal to or even lower than formaldehyde emissions from non-catalyst equipped gasoline-fueled vehicles, but higher than formaldehyde emissions from catalyst equipped gasoline-fueled vehicles.

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Table 1

Process Efficiencies and Product Mix
of Various Coal Liquefaction Processes

<u>Process</u>	<u>Conversion Efficiency</u>	<u>Product Mix (Energy Basis)</u>
Crude Petroleum	92%	50% Gasoline 33% Distillate 15% Residual 2% LPG
<u>Indirect Liquefaction</u>		
Modified Lurgi Gas. Lurgi Synthesis	57.3%	100% MeOH*
Koppers Totzek Gas. ICI Synthesis	49.3%	100% MeOH*
Mobil MTG		
Fixed Bed	43-50%	88% Gasoline
Fluidized Bed	45-53%	12% LPG
<u>Direct Liquefaction**</u>		
Exxon Donor Solvent (EDS)	55.8%	32.7% Reg. Gasoline 14.0% Prem. Gasoline 25.6% No.2 Fuel Oil 9.6% LPG 18.1% SNG
H-Coal	61.8%	33.1% Reg. Gasoline 11.2% Prem. Gasoline 20.4% No.2 Fuel Oil 22.3% LPG 13.0% SNG
Solvent Refined Coal (SRC) II	63.6%	64.7% Gasoline 12.1% LPG 23.2% SNG

* MeOH = 95-98% methanol, 1-3% water and the remainder higher alcohols.

** These efficiencies include the effect of refining where needed. However, the refinery product slates are not identical for each of the direct liquefaction processes.

Table 2

Product and Capital Costs of Coal
Liquefaction Processes (1981 Dollars)

Liquefaction Process	Product Mix	Product Cost (\$/mBtu)		Capital Cost** (Billions of Dollars)
		11.5%	30%	
		CCR	CCR	
<u>Direct</u>				
EDS (Bit.)	32.7% Reg. Gas.	\$10.00	\$17.29	\$2.65
	14.0% Prem. Gas.	10.80	18.67	
	25.6% Fuel Oil	8.20	14.18	
	9.6% LPG	7.70	13.31	
	18.1% SNG	8.00	13.83	
H-Coal (Bit.)	33.1% Reg. Gas.	7.79	14.97	3.30
	11.2% Prem. Gas.	8.37	16.09	
	20.4% Fuel Oil	6.38	12.27	
	22.3% LPG	6.00	11.52	
	13.0% SNG	6.23	11.97	
SRC-II (Bit.)	64.7% Gasoline	9.87	19.06	3.40
	12.1% LPG	7.60	14.68	
	23.2% SNG	7.90	15.24	
<u>Indirect</u>				
Texaco (Bit.)	100% MeOH*	5.90-	9.44-	1.99-
		6.48	10.41	
Koppers (Bit.)	100% MeOH*	7.23	12.42	2.92
Lurgi (Subbit.)	47.9% MeOH*	7.04	12.48	2.59
	49.7% SNG	5.63	9.93	
	2.4% Gasoline	7.04	12.48	
Modified Winkler (Lignite)	100% MeOH*	5.70	9.56	2.17
Lurgi Mobil MTG (Subbit.)	41.2% Reg. Gas.	8.01	14.35	2.95
	53.3% SNG	6.41	11.48	
	5.5% LPG	6.25	11.20	
Mobil MTG Incremental Cost	85-90% Reg. Gas. 10-15% LPG	1.45	2.87	0.68

* MeOH = 95-98% methanol, 1-3% water, and the remainder higher alcohols.

** Capital costs are instantaneous costs and do not include refinery capital costs.

Table 3

Vehicle Use Economics

	<u>Indirect Coal Liquefaction</u>		<u>Direct Coal Liquefaction</u>
	<u>Methanol</u>	<u>Gasoline (Mobil MTG)</u>	<u>Gasoline</u>
Cost at Pump* (\$ per mBtu)	7.60-14.30	8.70-16.60	9.10-20.40
Annual Savings (Or Cost) Relative to MTG Gasoline, \$**	23-243	0	(20-172)

* Range of plantgate cost is the lowest cost using the low CCR and the highest cost using the high CCR, all using bituminous feedstocks.

** Includes conservative assumptions for methanol: 1) only 20% improved engine efficiency over gasoline, and 2) the same engine cost as gasoline engines.

Table 4

Average Light-Duty Vehicle
Emission And Energy Efficiency Results

	Federal Test Procedure			
	Ford Escorts		VW Rabbits	
	Gas[a]	Meth[b]	Gas	Meth
Hydrocarbons (FID), g/mi	0.37	0.42[c]	0.11	0.39[c]
Carbon Monoxide, g/mi	4.49	6.03	1.08	0.88
Oxides of Nitrogen, g/mi	0.55	0.40	0.16	0.68
Particulate, mg/mi	9.2	6.3	11.8	4.7
Methanol, mg/mi	ND[d]	407	ND	440
Total Aldehydes and Ketones, mg/mi	0.2	33.6	ND	10.3
Formaldehyde, mg/mi	0.2	33.0	ND	10.3
Total Individual Hydrocarbons, mg/mi	155	50	40	5
Methane, mg/mi	96.1	48.3	14.0	4.8
Ethylene, mg/mi	8.7	0.3	4.8	0.2
Ethane, mg/mi	18.2	0.5	2.6	0.1
Acetylene, mg/mi	1.4	0.1	1.8	0.1
Propane, mg/mi	0.8	0.6	ND	ND
Propylene, mg/mi	6.1	ND	4.2	ND
Benzene, mg/mi	6.3	0.1	5.3	ND
Toluene, mg/mi	17.2	0.1	9.2	ND
Nitrosamines, mg/mi	ND	ND	ND	ND
Ammonia, mg/mi	[e]	10.0	[e]	[e]
Total Cyanide, mg/mi	[e]	ND	[e]	[e]
Total Organic Amines, mg/mi	[e]	0.1	[e]	[e]
Methyl Nitrite, ppm	[e]	0-0.5	ND	0-1.1
Energy Efficiency, mi/10 ⁴ Btu	2.16	2.25	2.10	2.46

[a] Gasoline-fueled.

[b] Methanol-fueled.

[c] Hydrocarbons as measured by the FID (flame ionization detector) and expressed as methanol.

[d] None detected.

[e] Analysis not conducted.

Table 5

Average Heavy-Duty Engine Emission
And Energy Efficiency Results Over
The Transient Federal Test Procedure

	Volvo Diesel TC*	MAN Diesel TC, IC*	MAN Methanol NA*
	No Cat	No Cat	W/Cat
Hydrocarbons, [a] g/hp-hr	0.85	0.85	0.04
Carbon Monoxide, g/hp-hr	3.01	3.16	0.31
Oxides of Nitrogen, [b] g/hp-hr	8.34	8.54	6.61
Particulate, g/hp-hr	0.52	0.37	0.04
Methanol, mg/hp-hr	[c]	[c]	680
Total Aldehydes and Ketones, mg/hp-hr	10	[d]	1
Formaldehyde, mg/hp-hr	10	[d]	1
Total Phenols, mg/hp-hr	26	[d]	0
Total Individual			
Hydrocarbons, mg/hp-hr	97	[d]	1
Methane, mg/hp-hr	11	[d]	1
Ethylene, mg/hp-hr	78	[d]	1
Ethane, mg/hp-hr	1	[d]	1
Acetylene, mg/hp-hr	2	[d]	1
Propylene, mg/hp-hr	6	[d]	1
Benzene, mg/hp-hr	1	[d]	1
Sulfate, mg/hp-hr	28	[d]	[c]
Benzo(a)pyrene, ug/hp-hr	2.8	[d]	0.01
Fuel Consumption			
lb diesel equivalent/hp-hr	0.476	0.451	0.538
Smoke, peak percent opacity	33	[d]	0

* NA = Naturally Aspirated, TC = Turbocharged, IC = Intercooled; the brake specific fuel consumption is directly affected by the technology employed with improvements expected in going from NA to TC to IC. Therefore, direct efficiency comparisons are not possible.

[a] Hydrocarbons as measured by the HFID (heated flame ionization detector) and expressed as diesel-like species.

[b] No NOx correction factor used.

[c] Does not apply.

[d] No analysis performed.

Table 6

Methanol Catalyst Preliminary Summary

<u>Catalyst</u>	<u>HC(FID)</u> <u>g/mi</u>	<u>CO</u> <u>g/mi</u>	<u>NOx</u> <u>g/mi</u>	<u>HCHO</u> <u>mg/mi</u>
No Catalyst	0.90	7.70	2.17	330
VW Stock - 0% O ₂	0.15	0.80	0.56	18
VW Stock - 3% O ₂	0.19	0.73	1.80	23
A - 0% O ₂	0.11	0.69	0.62	12
A - 3% O ₂	0.12	0.39	2.01	16
B - 0% O ₂	0.13	0.77	0.76	11
B - 3% O ₂	0.13	0.40	2.05	14
C - 0% O ₂	0.15	1.47	0.85	30
C - 3% O ₂	0.16	0.35	2.07	73
D - 0% O ₂	0.17	1.99	0.74	42
D - 3% O ₂	0.14	0.38	1.98	68
E - 0% O ₂	0.28	2.85	1.97	-*
E - 3% O ₂	0.28	2.05	1.95	-

* Results not complete.

Table 7

Comparison of Average FTP Formaldehyde Emissions
for Various Light-Duty Vehicles

	<u>HCHO Emissions</u> <u>(mg/mile)</u>
<u>Gasoline-Fueled Vehicles</u>	
1981 3-way-catalyst equipped cars	1
1978, 1979 3-way-catalyst equipped cars	2
1978 oxidation-catalyst equipped cars	3-11
1977 non-catalyst cars	16
1970 non-catalyst cars	51
<u>Methanol-Fueled Vehicles</u>	
1981 3-way-catalyst equipped, carbureted car (Escort)	33
1981 3-way-catalyst equipped, fuel injected car (Rabbit)	10

Figure 1

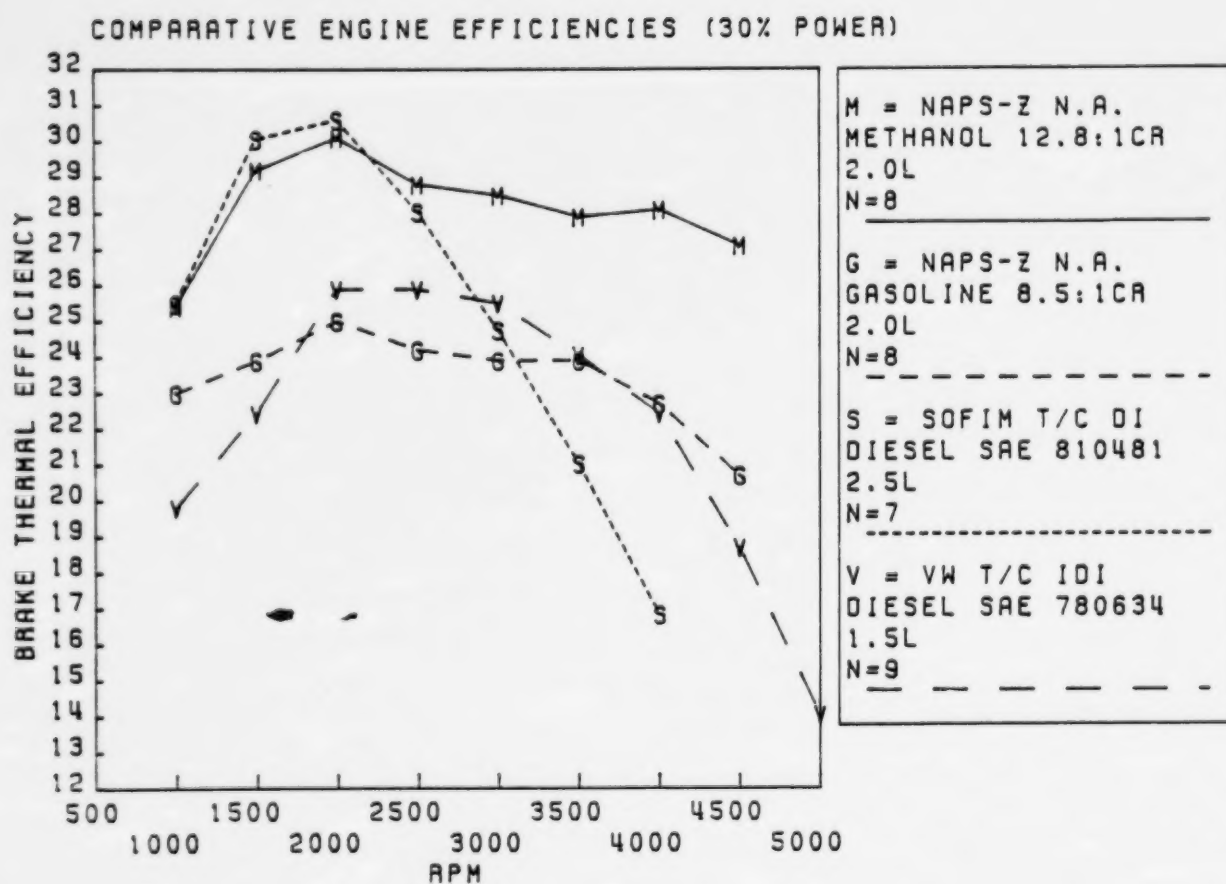


Figure 2

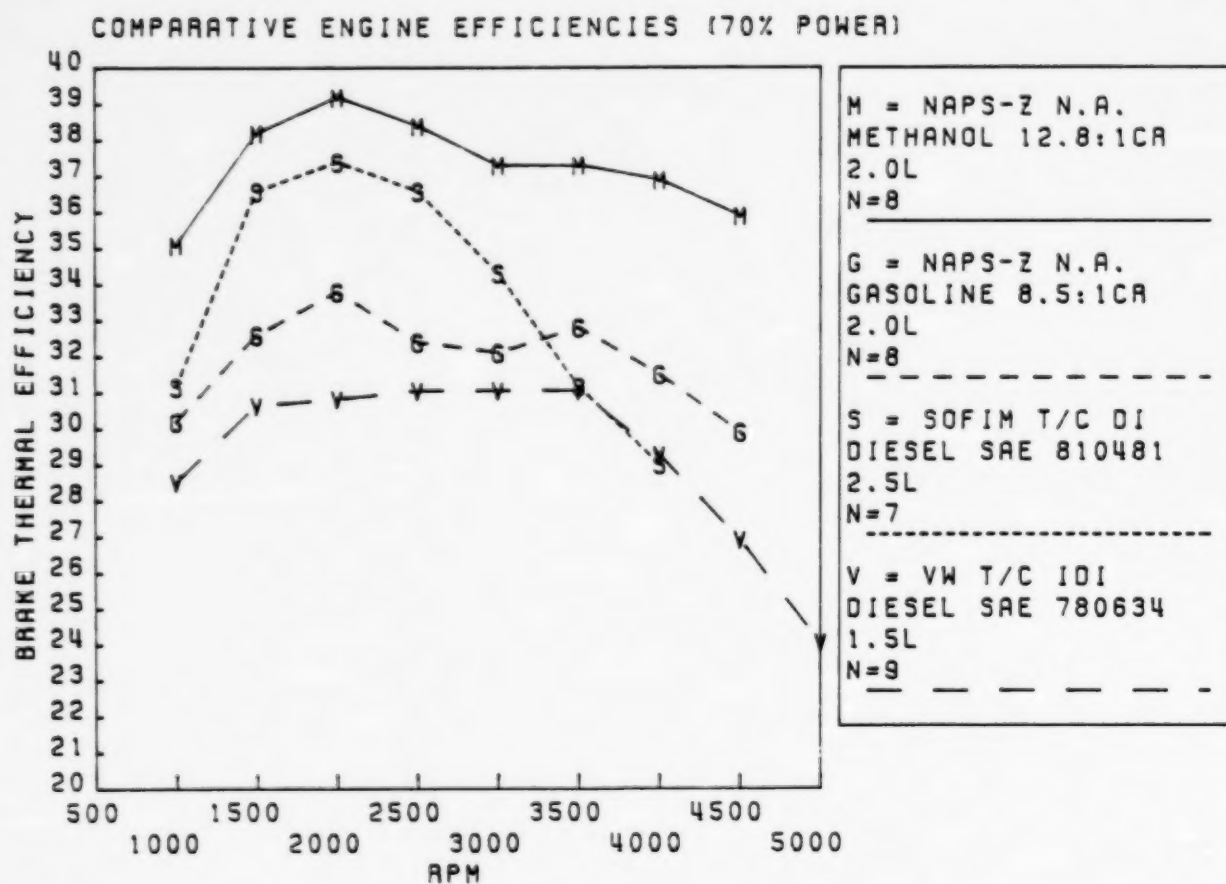


Figure 3

HRCC ENGINE RESULTS 20REV/S 1.5 BMEP BAR

x METHANOL
 ◇ 98RON GASOLINE

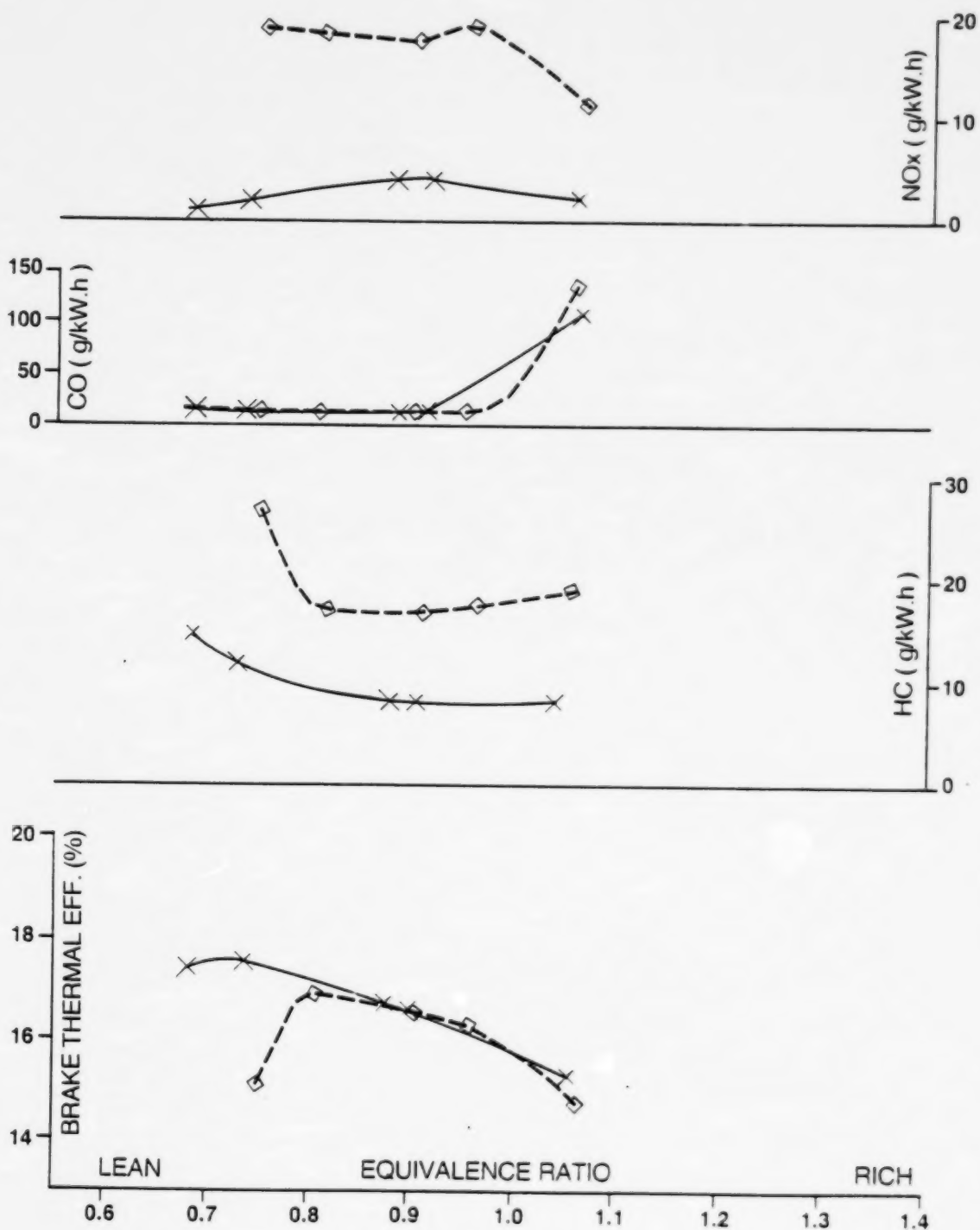


Figure 4

**HRCC ENGINE RESULTS
60REV/S 4.0 BMEP BAR**

X — X METHANOL
 ◇ — ◇ 98RON GASOLINE

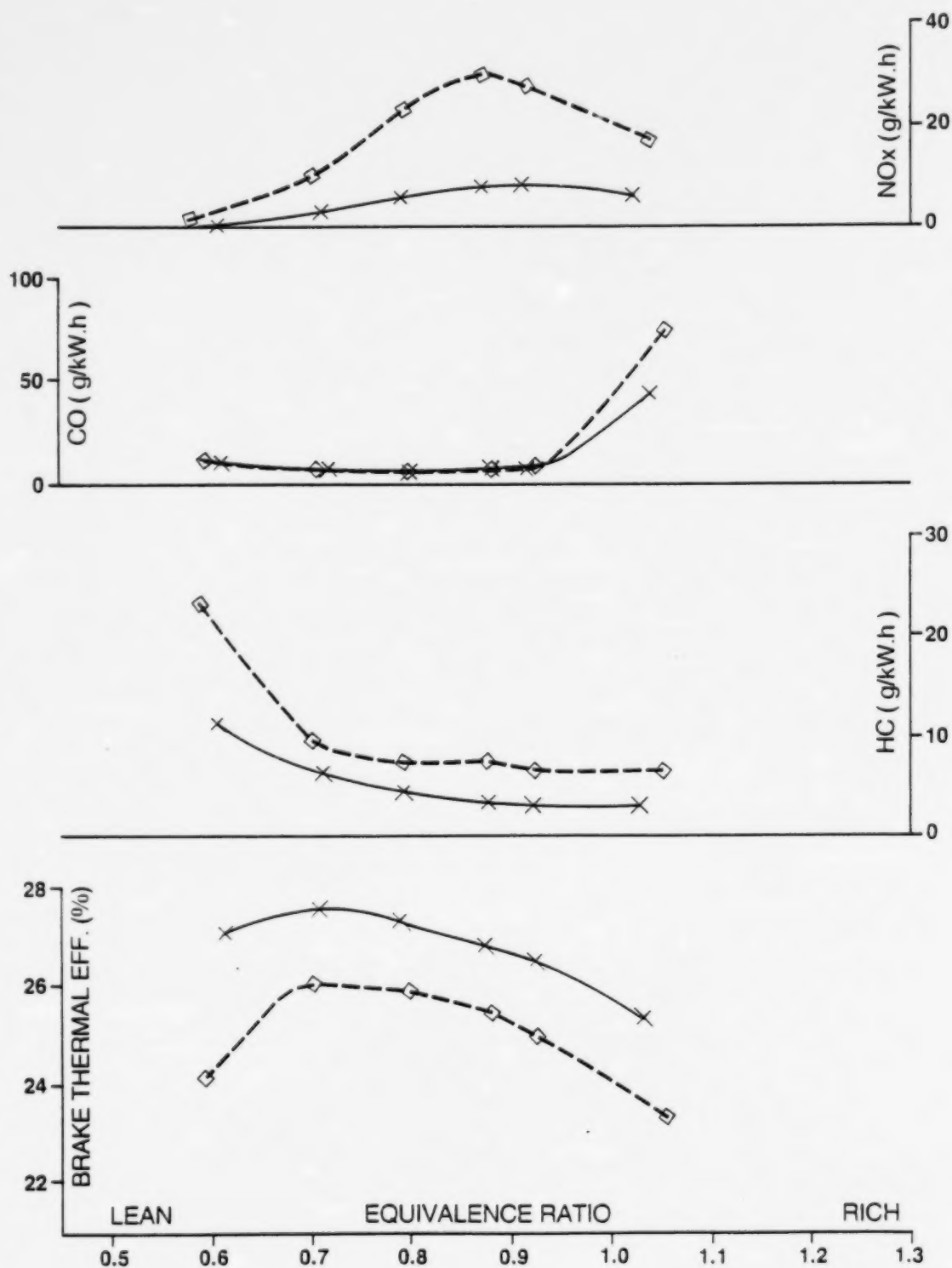


Figure 5

HRCC IDLE TESTS—900 RPM

- 1.5L HRCC engine—Gasoline
- △ 1.6L Standard engine—Gasoline
- × 1.5L HRCC Engine—Methanol (Gasoline Energy-Equivalent results)

